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by

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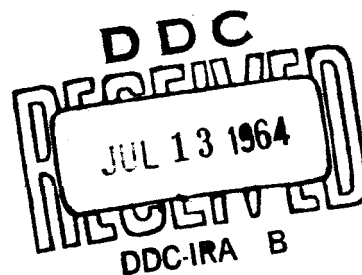WIS-TCI-52   9 June 1964

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I. Introduction

Ignoring spins, the canonical procedure for introducing a static magnetic field into the electronic Hamiltonian

$$H_0 = \sum_j \frac{1}{2m} \vec{P_j} \cdot \vec{P_j} + V \equiv T + V \tag{1}$$

is to make a substitution for $\vec{P_j}$

$$\vec{P_j} \longrightarrow \vec{P_j} + \frac{q}{c} \vec{A}(\vec{r_j}) \tag{2}$$

where $\vec{A}$ is the vector potential and q is the electronic charge (>0). This substitution yields the Hamiltonian

$$H = H_0 + H_1 + H_2 \tag{3}$$

where

$$H_1 = \sum_j \frac{1}{2m} \frac{q}{c} \left(\vec{P_j} \cdot \vec{A}(\vec{r_j}) + \vec{A}(\vec{r_j}) \cdot \vec{P_j} \right) \tag{4}$$

and

$$H_2 = \sum_j \frac{1}{2m} \left(\frac{q}{c} \right)^2 \vec{A}(\vec{r_j}) \cdot \vec{A}(\vec{r_j}) \tag{5}$$

The replacement (2) is said to be a gauge invariant one in that a subsequent gauge transformation on A:[1]

$$\vec{A}(\vec{r_j}) \longrightarrow \vec{A}(\vec{r_j}) + \vec{\nabla}_j \Lambda \tag{6}$$

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[1] Here Λ can be any real function of the particle coordinates. In what follows we will refer to a __proper__ gauge transformation if Λ takes the special form $\Lambda = \sum_j \lambda(\vec{r_j})$

so that (6) becomes

$$\vec{A}(\vec{r}_j) \longrightarrow \vec{A}(\vec{r}_j) + \vec{\nabla}_j \chi(\vec{r}_j)$$

corresponding to a real electromagnetic gauge transformation

$$A(\vec{r}) \longrightarrow \vec{A}(\vec{r}) + \vec{\nabla}\chi(\vec{r})$$

can be undone by a unitary transformation and hence has no effect on the energy eigenvalues.[2] Namely, the effect of the transformation (6) is to replace H by

$$H' = H_0 + H_1' + H_2' \tag{7}$$

where H_1' and H_2' are derived from H_1 and H_2 by the substitution (6). One then readily shows that

$$H' = U^\dagger H U \tag{8}$$

where

$$U = e^{i \frac{q}{\hbar c} \Lambda} \tag{9}$$

is clearly a unitary operator if we assume[1], as Λ is real

Usually the main point made in deriving (8) is the proof that

$$U^\dagger \left(\vec{P}_j + \frac{q}{c} \vec{A}(\vec{r}_j) \right) U = \vec{P}_j + \frac{q}{c} \vec{A}(\vec{r}_j) + \frac{q}{c} \vec{\nabla}_j \Lambda$$

which, of course, is true. We would like here to emphasize another point - the proof of (8) also involves showing that

$$U^\dagger V U = V \tag{*}$$

For a local potential, i.e., if $V\psi = V(\vec{r}_1 \cdots \vec{r}_n) \psi(\vec{r}_1 \cdots \vec{r}_n)$

this is trivial. For a non-local potential

$$V\psi = \int (\vec{r}_1 \cdots \vec{r}_n | V | \vec{r}_1' \cdots \vec{r}_n') \psi(\vec{r}_1' \cdots \vec{r}_n') \, d\vec{r}_1' \cdots d\vec{r}_n'$$

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[2] This last statement assumes that the unitary transformation is consistent with boundary and regularity conditions. See Y. Ahranov and D. Bohm, Phys. Rev. 115, 485 (1959), and R. C. Jaklevic, et al, Phys. Rev. Lett 12, 274 (1964).

it is false. We discuss this further in the next section.

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II. Non-Local Potentials

First of all let us note that such potentials do occur both explicitly and implicitly:

(A) In the coupled (unrestricted) Hartree-Fock method[3]

(B) In the uncoupled Hartree-Fock method[3]

(C) In any one-electron theory for which the zero field one-electron orbitals are not all eigenfunction of a single local one-electron Hamiltonian[4].

Now for a non-local potential, ($\maltese$) implies

$$e^{-\frac{i}{\hbar}\Lambda(\vec{r}_1\cdots\vec{r}_n)}(\vec{r}_1\cdots\vec{r}_n|V|\vec{r}_1'\cdots\vec{r}_n')e^{\frac{i}{\hbar}\Lambda(\vec{r}_1'\cdots\vec{r}_n')} = (\vec{r}_1\cdots\vec{r}_n|V|\vec{r}_1'\cdots\vec{r}_n')$$

which is in general false (unless V is local, i.e.,

$$(\vec{r}_1\cdots\vec{r}_n|V|\vec{r}_1'\cdots\vec{r}_n') \sim \delta(\vec{r}_1-\vec{r}_1')\cdots\cdots\delta(\vec{r}_n-\vec{r}_n')\, ,$$

Thus we conclude that if H_0 contains a non-local potential then when we introduce a magnetic field we must, in addition to the substitution (2),

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[3] See A. Dalgarno, Adv. in Phys. $\underline{11}$, 281 (1962) for an explanation of the terminology.

[4] Given N orthogonal one-electron functions Ψ_L, then in general there is no local V such that $\left(-\frac{\hbar^2}{2m}\nabla^2 +V\right)\Psi_L = \epsilon_L\Psi_L$ for all L. However, one can always find a non-local V (see S.T. Epstein, J. Chem. Phys. to be published).

make a substitution[5]

$$\mathbb{V} \rightarrow \mathbb{V}_A$$

in such a way that under a further gauge transformation (6), where $\mathbb{V}_A \rightarrow \mathbb{V}_A'$

$$\mathbb{V}_A' = \mathbb{U}^\dagger \, \mathbb{V}_A \, \mathbb{U}$$

One immediate consequence of this discussion is that the

uncoupled Hartree-Fock approximation is intrinsically not gauge

invariant since the non-local potential is fixed independently of

the magnetic field.

Further, other one-electron theories of magnetism (Pople, Hameka,

Karplus, etc.) may or may not be intrinsically gauge invariant

depending on the choice of unperturbed orbitals[4,6].

On the other hand (as is known, at least for special cases[7]) the

coupled (unrestricted) Hartree-Fock theory is invariant to proper

gauge transformations just because the non-local potential does

respond to the magnetic field. We will give an elegant proof of this

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[5] There are many ways of doing this. We will not discuss this
further here. See Y. Yamaguchi, Phys. Rev. 95, 1628 (1957),
section 4 and references given there.

[6] Such theories often involve many other approximations (See for
example the exchange between H. F. Hameka and J. A. Pople, J. Chem.
Phys. 37, 3008, 3009 (1962)). It would be interesting to test these
on the one-electron 2-coulomb-center problem where accurate
analytical calculations seem feasible.

[7] See for example, R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb,
J. Chem. Phys. 38, 550 (1963).

in the next section. A direct proof follows from the observation that

the non-local part of the one-electron Hamiltonian is just

$$\langle \vec{r} | \, \upsilon_A | \vec{r}' \rangle = \sum_{M} \varphi_M(\vec{r}) \, \varphi_M^{*}(\vec{r}') \big/ | \vec{r} - \vec{r}' |$$

Now under the transformation (8) wave functions change according to

$$\psi' = U^{\dagger} \psi$$

so that, specializing to a one-electron problem with $U = e^{i \frac{e}{\hbar c} \lambda(\vec{r})}$

we have

$$\langle \vec{r} | \, \upsilon_A' | \vec{r}' \rangle = \sum_{M} \varphi_M'(\vec{r}) \, \psi_M'^{*}(\vec{r}') \big/ | \vec{r} - \vec{r}' |$$
$$= e^{-i \frac{e}{\hbar c} \lambda(\vec{r})} \, \langle \vec{r} | \upsilon_A | \vec{r}' \rangle \, e^{i \frac{e}{\hbar c} \lambda(\vec{r}')}$$

or

$$\upsilon_A' = U^{\dagger} \, \upsilon_A \, U \quad .$$

III. <u>Gauge Invariance of Variational Calculations</u>

In a general way one can ask the question, under what circum-

stances will the variational principle $\delta J = 0$ where

$$J = (\tilde{\psi}, (H - \tilde{E}) \tilde{\psi})$$

yield the same energy as the variation principle $\delta J' = 0$ where

$$J' = (\tilde{\psi}, (H' - \tilde{E}') \tilde{\psi})$$

and where we use the <u>same</u> set of trial function $\tilde{\psi}$? Using (8)

to write

$$J' = (U \tilde{\psi}, (H - \tilde{E}') U \tilde{\psi})$$

we have the answer: A sufficient condition for invariance to the gauge transformation U is that the set of trial functions $\mathsf{U}\tilde{\psi}$ be identical to the set $\tilde{\psi}$. As an immediate consequence we have the gauge invariance of the exact solution (the set $\tilde{\psi}$ includes "all functions") and the invariance of unrestricted Hartree-Fock solution to proper gauge transformations (if $\tilde{\psi}$ is a determinant so is $\mathsf{U}\tilde{\psi}$ when Λ is a proper gauge transformation[1]).

Now let us suppose that for some class of gauge transformations, depending say on arbitrary parameters or arbitrary functions, it is not true that the set $\mathsf{U}\tilde{\psi}$ is the same as the set $\tilde{\psi}$. Then we may ask, among the set of gauges under consideration, is there some optimal gauge in which to do the calculation?[9] The answer which suggests itself is - choose the gauge such that small variations around it yield no variation in $\tilde{E}'$, i.e., require a sort of local or first order gauge invariance within the set of gauges under consideration. Thus we require

$$(\tilde{\psi}, \delta H' \tilde{\psi}) = 0 \qquad (12)^{10}$$

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[8] Here $\tilde{\psi}$ is a trial function, and $\tilde{E}$ the trial energy. The variation is to be carried out with $\tilde{E}$ fixed. $\tilde{E}$ is then determined from $J=0$.

[9] This question has been discussed by many people, mainly in a semi-empirical fashion. See for example reference 7.

[10] This condition ensures local gauge invariance to all orders in the field. Since usually one is interested in at most second order in the field, a perturbation analysis of (12) would be appropriate. We will not pursue this here.

in addition to the usual

$$(\delta\tilde{\Psi}, (H' - \tilde{E}')\tilde{\Psi}) = 0 \quad \text{And} \quad (\tilde{\Psi}, (H' - \tilde{E}')\delta\tilde{\Psi}) = 0 \qquad (13)$$

which follow from $\delta J' = 0$

Another question now arises - to what extent is the result of this procedure actually gauge invariant, i.e., independent of the $\vec{A}$ from which we started? The answer follows directly from the observation that (12) and (13) are equivalent to

$$\delta(U\tilde{\Psi}, (H - \tilde{E}')U\hat{\Psi}) = 0 \qquad (14)$$

where we vary both U And $\tilde{\Psi}$. From the discussion at the beginning of this section it follows then that our results will be invariant to a further gauge transformation

$$\vec{A}(\vec{r}_j) \rightarrow \vec{A}(\vec{r}_j) + \vec{\nabla}_j \Lambda'$$

if the set $U'U\tilde{\Psi}$ is the same as the set $U\tilde{\Psi}$.

IV. Connections with other work.

In this section we wish to make connections between eq. (12) and results proved by other authors, principally Rebane[11]; Das and Bersohn[12] and Karplus and Kolker[13].

[11] T. K. Rebane, J.E.T.P., 11, 694 (1960).

[12] T. P. Das and R. Betsohn, Phys. Rev., 115, 895 (1959). References to earlier works by other authors are also given in this paper.

[13] M. Karplus and H. Kolker, J. Chem. Phys., 38, 1263 (1963).

(A) Not surprisingly eq. (12) is equivalent to a hypervirial theorem[14]. Namely, from (8) and (9) one readily derives

$$\delta H' = \frac{i\phi}{\hbar c} [H', \delta \Lambda]$$

whence (12) becomes

$$(\tilde{\Psi}, [H', \delta\Lambda] \tilde{\Psi}) = 0 \qquad (15)$$

(B) <u>We now restrict ourselves to situations in which the set $\tilde{\Psi}$ consists of a single fixed (i.e. not to be varied), real function</u> and in which V is local so that H' is correctly given by (7). Thus (12) can be written

$$\delta(\Psi_0, H' \Psi_0) = 0 \qquad (16)$$

We now show that this is Rebane's variation principle. Namely, since H_0 is fixed $\delta(\Psi_0, H_0 \Psi_0) \cong 0$. Further H_1' is a pure imaginary Hermitian operator whence, if Ψ_0 is real, $(\Psi_0, H_1' \Psi_0) \cong 0$ Thus (16) becomes

$$\delta(\Psi_0, H_2' \Psi_0) = 0 \qquad (17)$$

which is exactly Rebane's principle (we may note, however, that in Rebane's discussion Ψ_0 was assumed to be the ground state eigenfunction of H_0). In words, we are instructed to choose the gauge in such a way as to minimize the diamagnetic energy contributions

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[14] S. T. Epstein and J. O. Hirschfelder, Phys. Rev. <u>123</u>, 1495 (1961). See especially footnote 3.

from H'.[15]

(C) Using the explicit form for H_2', arbitrary variation of Λ in (16) leads to a differential equation for Λ - Rebane's differential equation. An interesting alternative derivation can be based on (15) with $\tilde{\Psi} = \Psi_0$: Since $\delta\Lambda$ is a function only of coordinates we have

$$[H_1', \delta\Lambda] = [H_0, \delta\Lambda] + [H_1', \delta\Lambda]$$

and since further $i[H_0, \delta\Lambda]$ is a pure imaginary Hermitian operator it follows that (15) becomes

$$(\Psi_0, [H_1', \delta\Lambda]\Psi_0) = 0$$

If this is to be true for arbitrary $\delta\Lambda$ it implies

$$H_1'\Psi_0 = 0$$

which is Rebane's equation.

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[15] See also S. I. Chan and T. P. Das., J. Chem. Phys. 37, 1527 (1962). In connection with their discussion note, however, that with our approximation $\tilde{E}' = (\Psi_0, H'\Psi_0) = (\Psi_0, H_0\Psi_0) + (\Psi_0, H_2'\Psi_0)$ i.e. we have only a diamagnetic contribution from H', though from H we get both paramagnetic and diamagnetic contributions (see (D) below).

(D)   Since H_2 is a fixed operator (17) can also be written

$$\delta \left(\psi_0, (H_2' - H_2) \psi_0 \right) = 0 \tag{18}$$

Then using the fact that Λ is a function only of coordinates one readily finds from (8) and (9) that

$$H_2' - H_2 = \frac{i\Phi}{\hbar c} [H_1, \Lambda] - \frac{1}{2} \left(\frac{\Phi}{\hbar c} \right)^2 [\Lambda, [\Lambda, H_0]]$$

whence (18) becomes

$$\delta \left(\psi_0, \left\{ \frac{i\Phi}{\hbar c} [H_1, \Lambda] - \frac{1}{2} \left(\frac{\Phi}{\hbar c} \right)^2 [\Lambda, [\Lambda, H_0]] \right\} \psi_0 \right) = 0 \tag{19}$$

If one now <u>assumes</u> that $H_0 \psi_0 = E_0 \psi_0$ then this is exactly the variation principle used by Das and Bersohn[12,16]. Namely, if one introduces $\tilde{\psi}^{(1)} \equiv \frac{i\Phi}{\hbar c} \Lambda \psi_0$ then (19) can be written in the more familiar form

$$\delta \left[(\psi_0, H_1 \tilde{\psi}^{(1)}) + (\tilde{\psi}^{(1)}, H_1 \psi_0) + (\tilde{\psi}^{(1)}, (H_0 - E_0) \tilde{\psi}^{(1)}) \right] = 0 \tag{20}$$

which is the form used by Das and Bersohn. As is well known it yields an upper bound (for the ground state) to $\epsilon^{(2)}$, the second order contribution of H_1 (the "paramagnetic" contribution).

However, although Das and Bersohn use (20) they do so with an

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[16] The relationship of the Das and Bersohn approach to the Rebane approach which we have found as a by-product of our investigation has been pointed out before. See, for example, S. K. Ghosh and S. K. Sinha, J. Chem. Phys. <u>36</u>, 737 (1962).

"approximate" ψ_0, one which is <u>not</u> an eigenfunction of H_0. Thus they do <u>not</u> calculate an upper bound to $\epsilon^{(2)}$ but only some less well controlled approximation to it[17]. Also, note that if ψ_0 is not "exact" then (19) is <u>not</u> equivalent to (20), and hence <u>not</u> equivalent to Das and Bersohn.

(E) For a general ψ_0, one which is not $\overset{necessarily}{\vee}$ an eigenfunction of H_0, (19) <u>is</u>, however, exactly the variation principle proposed by Karplus and Kolker[13]. To see this we remark that we can always consider ψ_0 to be the eigenfunction of a Hamiltonian $\mathcal{H}_0 = T + V_0$ with eigenvalue $\mathcal{E}_0$ where V is local [See R. Sternheimer, Phys. Rev. <u>96</u>, 951 (1954)]. Then since $[\Lambda, \mathcal{H}_0] =$

$$[\Lambda, T] = [\Lambda, \mathcal{H}_0] \text{ it follows that eqn. (19)}$$

<u>is</u> equivalent to a result of the form (20) but with H_0 and $\mathcal{E}_0$ replaced by $\mathcal{H}_0$ and $\mathcal{E}_0$ respectively. Thus what we would calculate from (19) would be an upper bound to the second order contributions of H_1 for the "atom" or "molecule" defined by $\mathcal{H}_0$. This is not an upper bound for the actual system but only some less well controlled approximation to it[18]. Indeed, it is exactly the approximation suggested by Karplus and Kolker.

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[17] The situation is somewhat confused by the fact that as, Das and Bersohn show, even with an approximate ψ_0, (20) may well have a minimum property (for the ground state). However, the point is that this minimum is <u>not</u> $\epsilon^{(2)}$, nor need it have any particular relation to $\epsilon^{(2)}$

[18] Note, however, that the approximate <u>total</u> energy $\tilde{E}'$ <u>is</u> an upper bound (for the ground state) to the exact <u>total</u> energy.